

~~This report has been prepared
for information and record
purposes and is not to be referenced
in any publication.~~

NATIONAL BUREAU OF STANDARDS REPORT

10 954

FIRE GROWTH AND FLASH FIRES IN A MODEL SIMULATING AN AIRCRAFT CABIN

III. ANALYSIS OF POLYURETHANE DECOMPOSITION PRODUCTS



U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

NATIONAL BUREAU OF STANDARDS

The National Bureau of Standards¹ was established by an act of Congress March 3, 1901. The Bureau's overall goal is to strengthen and advance the Nation's science and technology and facilitate their effective application for public benefit. To this end, the Bureau conducts research and provides: (1) a basis for the Nation's physical measurement system, (2) scientific and technological services for industry and government, (3) a technical basis for equity in trade, and (4) technical services to promote public safety. The Bureau consists of the Institute for Basic Standards, the Institute for Materials Research, the Institute for Applied Technology, the Center for Computer Sciences and Technology, and the Office for Information Programs.

THE INSTITUTE FOR BASIC STANDARDS provides the central basis within the United States of a complete and consistent system of physical measurement; coordinates that system with measurement systems of other nations; and furnishes essential services leading to accurate and uniform physical measurements throughout the Nation's scientific community, industry, and commerce. The Institute consists of a Center for Radiation Research, an Office of Measurement Services and the following divisions:

Applied Mathematics—Electricity—Heat—Mechanics—Optical Physics—Linac Radiation²—Nuclear Radiation²—Applied Radiation²—Quantum Electronics³—Electromagnetics³—Time and Frequency³—Laboratory Astrophysics³—Cryogenics³.

THE INSTITUTE FOR MATERIALS RESEARCH conducts materials research leading to improved methods of measurement, standards, and data on the properties of well-characterized materials needed by industry, commerce, educational institutions, and Government; provides advisory and research services to other Government agencies; and develops, produces, and distributes standard reference materials. The Institute consists of the Office of Standard Reference Materials and the following divisions:

Analytical Chemistry—Polymers—Metallurgy—Inorganic Materials—Reactor Radiation—Physical Chemistry.

THE INSTITUTE FOR APPLIED TECHNOLOGY provides technical services to promote the use of available technology and to facilitate technological innovation in industry and Government; cooperates with public and private organizations leading to the development of technological standards (including mandatory safety standards), codes and methods of test; and provides technical advice and services to Government agencies upon request. The Institute also monitors NBS engineering standards activities and provides liaison between NBS and national and international engineering standards bodies. The Institute consists of a Center for Building Technology and the following divisions and offices:

Engineering Standards Services—Weights and Measures—Invention and Innovation—Product Evaluation Technology—Electronic Technology—Technical Analysis—Measurement Engineering—Fire Technology—Housing Technology⁴—Federal Building Technology⁴—Building Standards and Codes Services⁴—Building Environment⁴—Structures, Materials and Life Safety⁴—Technical Evaluation and Application⁴.

THE CENTER FOR COMPUTER SCIENCES AND TECHNOLOGY conducts research and provides technical services designed to aid Government agencies in improving cost effectiveness in the conduct of their programs through the selection, acquisition, and effective utilization of automatic data processing equipment; and serves as the principal focus within the executive branch for the development of Federal standards for automatic data processing equipment, techniques, and computer languages. The Center consists of the following offices and divisions:

Information Processing Standards—Computer Information—Computer Services—Systems Development—Information Processing Technology.

THE OFFICE FOR INFORMATION PROGRAMS promotes optimum dissemination and accessibility of scientific information generated within NBS and other agencies of the Federal Government; promotes the development of the National Standard Reference Data System and a system of information analysis centers dealing with the broader aspects of the National Measurement System; provides appropriate services to ensure that the NBS staff has optimum accessibility to the scientific information of the world, and directs the public information activities of the Bureau. The Office consists of the following organizational units:

Office of Standard Reference Data—Office of Technical Information and Publications—Library—Office of International Relations.

¹ Headquarters and Laboratories at Gaithersburg, Maryland, unless otherwise noted; mailing address Washington, D.C. 20234.

² Part of the Center for Radiation Research.

³ Located at Boulder, Colorado 80302.

⁴ Part of the Center for Building Technology.

NATIONAL BUREAU OF STANDARDS REPORT

NBS PROJECT

4619193

October 1972

NBS REPORT

10 954

FIRE GROWTH AND FLASH FIRES IN A MODEL SIMULATING AN AIRCRAFT CABIN

III. ANALYSIS OF POLYURETHANE DECOMPOSITION PRODUCTS

by
Maya Paabo
and
J. J. Comeford
Center for Building Technology

Prepared for
Federal Aviation Administration
National Aviation Facilities Experimental Center



U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

TABLE OF CONTENTS

LIST OF FIGURES	i
LIST OF TABLES	ii
ABSTRACT	iii
1.0 INTRODUCTION	1
2.0 FLASH FIRE CELL	2
2.1 Design Criteria	2
2.2 Laboratory Model Construction	3
2.3 Ignition Source	3
2.4 Pyrolysis Unit	4
3.0 TEST PROCEDURES	4
3.1 Materials	5
3.2 Pyrolysis and Combustion Gas Analysis	7
3.3 Gas Chromatographic Equipment	7
3.4 Infrared Analysis	9
4.0 EXPERIMENTAL RESULTS	9
4.1 Combustible Gas Analysis	10
4.2 Gas Analysis	10
4.3 Analysis of Smoke	15
4.4 Intercomparison of Materials - Flash Fire Potential	19
5.0 SUMMARY OF RECOMMENDATIONS	19
5.1 Gas Analysis and Smoke Characterization	19
5.2 Development of Flash Fire Cell	20
6.0 REFERENCES	22

LIST OF FIGURES

- Figure 1 Schema of flash fire cell.
- Figure 2 Total combustible gases evolved from polyurethane foam heated in nitrogen as a function of temperature.
- Figure 3 Chromatograms of flexible foam decomposition products in air before onset of flash fire.
- Figure 4 Chromatogram of same mixture as Figure 3, but with "air" peak resolved only.
- Figure 5 Pyrogram of orange smoke deposit from flexible urethane.
- Figure 6 Pyrogram of acetone extract of orange smoke deposit.
- Figure 7 Pyrogram of original unretarded urethane foam.
- Figure 8 Infrared spectrogram of smoke condensate in KBr.
- Figure 9 Infrared spectrogram of acetone extract of smoke condensate in KBr.
- Figure 10 Infrared spectrogram of acetone extract of smoke condensate in CCl_4 .

LIST OF TABLES

1. Weight Percent Composition of Polyurethane Pyrolysis Products.
2. Polyurethane Pyrolysis Products.
3. Lower Limits of Flammability of Pyrolysis Products in Air.
4. Elemental Analysis of the Orange Smoke and Polyurethane Foam.
5. Intercomparison of Materials - Flash Fire Potential.

FIRE GROWTH AND FLASH FIRES
IN
A MODEL SIMULATING AN AIRCRAFT CABIN

Maya Paabo and J. J. Comeford

A laboratory model of a flash fire cell using a high voltage arc as an ignition source was assembled and tested. The cell is designed to pyrolyze the sample in air while measuring the time of onset of a flash fire and simultaneously allowing withdrawal of gas samples for analysis. Some of the low molecular weight products produced from the pyrolysis of flexible polyether type urethane foams were identified. The flash fire cell was used to compare the flash fire potential of polymers of potential interest to the aircraft industry. Studies of the role of smoke in flash fire produced in the pyrolysis of flexible urethanes were undertaken. Flash fires in the cell were recorded on 16 mm motion picture film.

1.0 Introduction

This report covers the time interval March 1971 through June 1972. Previous NBS reports on the first phase of this program described exploratory experiments on fire growth in model enclosures [1,2] and an extensive investigation of smoke and gases produced by testing aircraft interior materials in the smoke test chamber [3]. While these data are helpful in evaluating potential hazards of various materials, the complex phenomena of flash fires as they might relate to aircraft cabins are not well defined. In this work, a flash fire appears to involve gas phase combustion reactions from the products of the thermal decomposition of solid organic materials within the cabin enclosure. The above studies on a gross macroscopic level have limited value in arriving at a detailed understanding of flash fires or flashover conditions [1,2,4,5]. Meaningful design of large scale tests requires some understanding of the fundamental processes involved and identification of the important variables. Carefully designed laboratory models should provide a practical approach to the analysis of these complex systems while affording the opportunity to obtain precise quantitative data on combustion products and reactions.

The initial reactions of interest in this study include a low temperature pyrolysis reaction in the condensed phase to

produce a combustible gas mixture. Subsequent pyrolysis of organic compounds in the gas phase may then occur. Propagation of flame in the gas phase will depend on the composition of the combustibles and ratio of combustibles to air. In addition to these important variables the rate of heating, source of ignition, and type of heating have been considered in designing a laboratory model. This report describes:

(a) the successful design and construction of a laboratory model for producing flash fires; (b) preliminary comparisons of various polymers to assess the usefulness of the apparatus for measuring flash fire potential of materials; and (c) the analysis of pyrolysis gases evolved from flexible polyurethane.

2.0 FLASH FIRE CELL

2.1 Design Criteria

Design criteria for the laboratory model included:

1. An arrangement for varying the method of heating the sample to be pyrolyzed. Methods considered included burner heating, electric furnace, and laser radiation.
2. Variable sources of ignition remote from the site of solid and gas pyrolysis.
3. Capability of monitoring gas composition during the experiment by means of infrared absorption spectrophotometry.

4. Sampling ports for removal of gas samples for analysis by means of gas chromatography with a minimum perturbation of the cell contents.
5. Transparent cell to allow measurement of flame front and time of initiation of flash fire.
6. Positional flexibility to allow measurement of the effect of orientation of the cell in gravitational field on the flash fire.

2.2 Laboratory Model Construction

The cell was constructed of a pyrex cylinder 50 cm in length and 5 cm in diameter (Figure 1). Each end of the glass cylinder had as an integral part "O" ring flanges filled with neoprene "O" rings and polymethyl methacrylate windows fastened with spring loaded clamps. This arrangement allowed for safe pressure release resulting from the explosions generally accompanying the flash fire. The pyrolysis sample holder (B) was connected to the main cell body by a glass "O" ring flange. The "O" ring connection facilitated rapid removal for cleaning and sample replacement. Fittings were provided for rapid gas sampling into evacuated bulbs (A,C,D) and for removal or adjustment of the ignition source (E).

2.3 Ignition Source

The ignition source was a 10 KV AC arc, about 1 cm in length, between copper or platinum electrodes.

2.4 Pyrolysis Unit

The pyrolysis chamber consisted of a pyrex glass cylinder closed at one end and fitted with an "O" ring flange at the other end (Figure 1). This allowed easy removal for cleaning and quick interchange when the chamber volume to sample weight ratio was changed. A special chamber equipped with a NaCl window was used in rapid heating experiments employing 10.6 μm laser radiation. The majority of experiments were accomplished using a 7 x 4 cm diameter chamber externally heated by a Bunsen burner or a 250 watt electric furnace. In a typical furnace experiment a weighed sample was placed in the side arm and connected to the cell. The electric furnace preheated to temperature was rapidly placed around the pyrolysis chamber. Sample temperatures during pyrolysis were estimated from calibration runs with a chromel-alumel thermocouple in conjunction with a recording potentiometer. Pyrolysis temperatures with burner heating were estimated to be 250-350°C and with the electric furnace 400-500°C. Temperature gradients as great as 100°C were observed between the container wall and center of the sample compartment with rapid electric heating.

3.0 TEST PROCEDURE

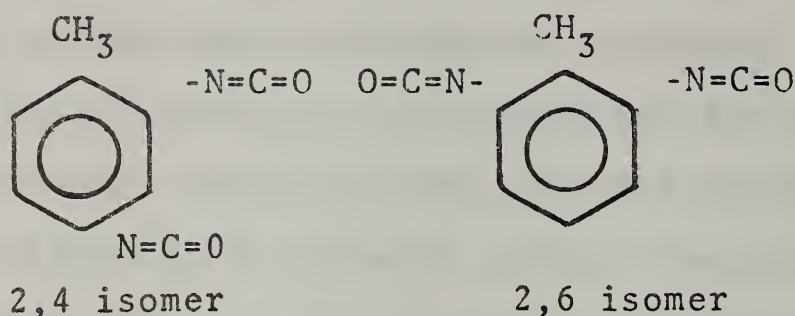
The test procedure was varied depending upon the purpose of the experiment. Initial evaluation of the cell was made by

preparing methane-air mixtures with the methane concentration just above the lower flammability limit [6]. A well defined blue flame front was observed to form at the ignition source and proceed the length of the cell in approximately 0.5 seconds. This rate was sufficiently slow to permit photography of the flame using conventional 16mm motion picture cameras. In a typical intercomparison experiment a 0.3g sample of polyurethane foam was placed in the side chamber and heated externally with either a burner or preheated electric furnace. The time of heating and the time of onset of a flash or explosion were recorded.

3.1 Materials

Due to the extensive use of flexible polyurethane type plastics in aircraft interiors, these polymers formed the basis for our initial investigation. The potential and real hazards associated with fires has been documented, for example, the BOAC fire in New York [7]. Urethane polymers vary widely in thermal and fire properties depending on the structure of the diisocyanate and polyhydroxyl compound polymerized plus other additives structurally and/or physically incorporated. Both fire retarded and unretarded foams were investigated. A specially prepared sample of urethane was obtained to represent a typical commercial formulation.

This was prepared from a blend of 80% 2,4 and 20% 2,6 toluene diisocyanate and a trifunctional polyether polyol in the presence of an amine catalyst. The monomer is an isocyanate, a compound containing the $-N=C=O$ group, in this case a diisocyanate, with two isocyanates per aromatic ring or per toluene molecule (methyl benzene) depicted as:



The polyol in this instance was a polymer formed from glycerol and ethylene oxide. The essential point is that it have a number of OH groups available to react with the isocyanate. The density of the foam was approximately 2.0 pounds per cubic foot (0.032 grams per cubic centimeter) and utilized water as a blowing agent. The foam was prepared from the following formulation: a trifunctional, 3000 m.w. polyether polyol (a propylene oxide adduct of glycerol water, a polydimethylsiloxane-polyoxyalkylene block copolymer, amine catalyst, stannous octoate, and a blend of 2,4 and 2,6 toluene diisocyanates.

The majority of tests where the urethane sample is not specified employed a polyether diisocyanate type urethane provided by the FAA. These were both fire retarded and unretarded

samples although the type of retardant was not identified. In tests where retarded samples received from FAA were employed no measureable differences from unretarded foam were noted. Since these samples had aged for several years the possibility of a fugitive retardant may account for the lack of difference.

3.2 Pyrolysis and Combustion Gas Analysis

Gas samples were collected both before and after flashover. A 500 ml evacuated bulb fitted with a hypodermic needle and rubber septum was used. Samples were then transferred through an evacuated manifold equipped with manometers to the sampling inlet valve of a gas chromatograph.

3.3 Gas Chromatographic Equipment

A gas chromatograph equipped with two thermal conductivity (TC) and two flame ionization detectors (FID), and two column ovens with temperature programming capabilities was used for separation and identification of the gaseous pyrolysis products. A sampling valve in conjunction with a 2 or 5 ml loop was used for transferring gas samples from the sampling bulb into the gas chromatograph.

The dual column gas chromatographic technique was used for simultaneous resolution of air components and low-boiling hydrocarbons. A 5 foot Porapak Q stainless steel column,

50/80 mesh, 1/4 inch in diameter was connected in series with a 5 foot molecular sieve 5A copper column, 60/80 mesh, 1/4 inch in diameter with the aid of a 4-way switching valve. The Porapak Q column was in one oven and during the analysis the temperature was programmed from 60 to 200°C by holding the column oven constant at 60°C for 4 minutes. Then the temperature was raised at a rate of 10°C/minute. Baseline drift during temperature programming was eliminated by using an identical reference column. Helium was used as a carrier gas at a flow rate of 60 ml/min. at 62 psi. The eluted gases were detected by one thermal conductivity and two flame ionization detectors held at 200°C. Since the first column did not resolve the air and methane peaks at these experimental conditions, the combined peak was allowed to enter the molecular sieve column and the 4-way valve was switched before heavier components, particularly carbon dioxide, were eluted from the Porapak Q column. A matching restriction valve consisting of a micro-meter valve was connected to the exit of the 4-way valve to eliminate excessive pressure change. The molecular sieve column was held isothermally in the second oven at 90°C and the permanent gases and methane were detected by the second thermal conductivity detector. During the preliminary runs the dual column facility was not available and the sample gas mixture entered directly into the molecular sieve column held at 75°C. The filament currents of the thermal conductivity detectors were kept constant at either 100 or 150 milliamperes. Two recorders, 1 millivolt full scale sensitivity, were used.

For analysis of nonvolatile samples the gas chromatograph was equipped with a pyrolysis unit consisting of an electrode with platinum-rhodium filament and a variable power supply. A temperature of 1000°C was used for pyrolyzing samples of polyurethane foam and solid particles of smoke in a helium atmosphere. These degradation products were separated by the Porapak Q column using the same temperature programming as for the previous gaseous products.

3.4 Infrared Analysis

For this work infrared absorption spectra were recorded by a spectrophotometer with a spectral range of 250-4000 cm^{-1} . For gaseous samples a 1 m gas cell was used. For solid samples either the KBr pellet technique or the liquid phase technique in CCl_4 (0.07 mm cell) was used.

4.0 EXPERIMENTAL RESULTS

Considerable emphasis was placed on analysis of pyrolysis gases leading up to the onset of a flash fire. Identification of the gas or gases responsible could be important in suggesting ways of reducing this hazard. Thermal decomposition of polyurethanes in air produces a complex mixture of gases and smoke. This report describes the analysis of components with molecular weight 50 or less evolved during the initial stages of decomposition.

4.1 Combustible Gas Analysis

Total combustible gas release as a function of temperature was obtained in a special apparatus designed for the purpose [8].¹ A sample of foam was heated in nitrogen at a constant rate and the gases swept through a combustible gas analyzer. The resulting curve shows the total combustible gas release as a function of temperature (Figure 2). Fine thermocouple wire is employed with some care being given to maintaining thermal contact with the sample so that the temperatures will reflect actual decomposition points. Small amounts of combustible gas are released at 290 and 320°C with most decomposition occurring at 410°C. The heating was not continued above 500°C.

4.2 Gas Analysis

The gaseous pyrolysis products evolved by heating flexible polyurethane foam samples in air, were analyzed before and after flashover phenomenon by gas chromatography and infrared spectroscopy. Typical chromatograms of a pyrolysis mixture before flashover are shown in Figures 3 and 4. Figure 3 contains in effect two chromatograms, the upper curve monitored with the flame ionization detector (FID) and the lower curve with the thermal conductivity detector (TC). The temperature scale represents the column temperature program and the times

¹Analysis performed by R. J. McCarter, Fire Technology Division, NBS.

are elution or retention times. Both detectors are required because of their differing responses to the various components. The numbers are attenuation factors by which each peak area must be multiplied to intercompare amounts of each component. However, the two separate curves may not be intercompared because of the vastly differing response factors of the two detectors to the same compound.

The chromatograms obtained of gaseous mixtures before and after flashover were found to be similar when intercompared. The differences are probably obscured by the continuous generation of pyrolysis products replacing those depleted during combustion. The experimental system at the present does not permit isolation of the pyrolysis compartment from the main chamber. Refinement of this design will be considered in the future.

For qualitative identification of permanent gases and major low molecular weight decomposition products a comparison of the retention data of the pyrolysis mixture was made with those of known compounds. Nine major products were detected and eight were identified as carbon monoxide, carbon dioxide, water, methane, ethylene and/or acetylene, ethane, propylene, and acetone. Of the numerous minor peaks hydrogen, propane and methanol were identified.

Infrared spectra provide a convenient method of urethane identification and have been extensively studied [9].

Characteristic absorptions for urethanes are observed at 6.5 μm (Amide II - NH deformation), 5.8 μm (Amide I - C=O stretch), and 3.0 μm (NH stretch). Polyether type urethanes (-C-O-C-) absorbing at 9.0 μm may be distinguished from polyester types (-C-O-C-) absorbing at 8.0 μm [10].

0

Positive identification of the organic components in a complex unknown gaseous mixture, however, cannot be made from gas chromatographic retention data alone. Infrared spectroscopy was used as the only ancillary technique available for further confirmation. Infrared spectra of pyrolysis mixtures before and after flashover were obtained. Identification of minor components was not possible because of their low concentrations in the sample which is predominantly air.

Quantitative estimates of the pyrolysis products were made by determination of the recorded peak areas on gas chromatograms and by comparing peak heights of respective compounds.

The accuracy and reproducibility of the sampling system was tested by flushing a mixture of 6.1% methane and 93.9% air through the flashover chamber and analyzing gas samples by the chromatographic technique. The peak areas of the molec-

ular sieve chromatograms were evaluated by means of a disc integrator. The area normalization method using thermal conductivity detector response factors for O_2 , N_2 , and CH_4 was used to yield true weight areas [11]. The average methane content of these determinations was $6.0\% \pm 0.3$.

Table 1 lists the weight percentage composition of the polyurethane pyrolysis products resolved by means of a molecular sieve column estimated by the normalization method above. Figures in parentheses are the concentrations estimated by the absolute calibration method. Pure gases were sampled at known pressures and the recorder response per torr of pressure was determined. These results, however, are somewhat scattered because of the wide range of extrapolations from the calibration standards and the uncertainty of the detector sensitivity from day to day.

The absolute calibration method includes detector sensitivity, which will vary for different compounds, and relates the experimentally obtained peak area of the chromatogram to the measured pressure of a given component. The absolute calibration method was used to check the normalization method. To facilitate analysis the normalization method, where the air peak including CH_4 is taken as 100%, and the concentrations of other minor organic components were ignored, was employed. Within experimental error the two sets of data appear to agree.

The quantities of other organic compounds resolved by the Porapak Q column and detected by the flame ionization detector which does not respond to air or water were estimated by normalizing the peak heights to that of methane. The results are listed in Table 2. At the bottom of Table 2 are listed the estimated ratios of carbon dioxide to air and the presence of water as detected by the thermal conductivity detector. The Porapak Q column did not resolve methane from air as monitored by the thermal conductivity detector and the concentrations of other organic components were near or below the limit of sensitivity of the thermal conductivity detector.

Tables 1 and 2 reveal that none of the lower molecular weight combustibles are present in concentrations approaching their lower limits of flammability in air listed in Table 3. The lower limit of flammability is defined as the critical concentration of a combustible gas in a mixture below which no ignition occurs. The values in Table 3, designated L_{25} , refer to combustible mixtures in air at atmospheric pressure and 25°C [6]. The relatively small experimental variations of temperature and pressure and the type of ignition source have been included when the concentrations of combustibles are compared to their lower limits of flammability. For sample 15, for example, we have in volume percent listing L_{25} first and weight percent found second: H_2 (4.0 trace), CH_4 (5.0, 0.1), CO (12.5, 1.8) and other hydrocarbons of Table 2 in much

lower concentrations. The concentrations reported in Table 2 are relative to CH_4 taken as 1 so that for sample 15 propylene is 0.49 of .1 or .05% for example. The weight percentages of O_2 include 1.3% argon which is not resolved from the O_2 by the molecular sieve column. The nitrogen-oxygen ratios may also be effected by varying amounts of nitrogen released by the sample.

4.3 Analysis of Smoke

As the heating of the urethane sample progresses with the evolution of the gases listed in Tables 1 and 2 a dark brown or orange smoke is evolved before flashover. Its possible importance in flash fires, suggested by the fact that flash fires in the cell do not occur in its absence, dictated additional tests.

During the experiments of determining the appropriate weight of a polyurethane foam sample that causes flashover in the 1 liter chamber without additional air intake, it was observed that in case the high voltage spark was placed above the sample compartment, no flashover occurred until the heavy orange smoke reached the ignition source. Also, no flashover occurred when a filter of glass wool was placed between the sample compartment and main chamber for trapping out most of the solid particles.

The technique selected for characterization of the condensed smoke particles involved flash pyrolysis of the sample in a stream of helium by a heated electric filament. This pyrolysis unit is an integral part of the gas chromatographic equipment and the record of resulting volatile fragments is commonly called a pyrogram.

Pyrolysis-gas chromatography has been used to identify urethane foams with pyrolysis in a quartz tube in the 650-1000°C temperature range [12]. Product identification required both infrared spectroscopy and mass spectrometry. The main pyrolysis products from polyether foams at 650°C would appear to be aliphatic ketones, ethers, or esters while at 850°C the primary products are aromatic ring compounds.

In an attempt to elucidate the structure of the orange smoke and to determine its contribution to the flashover phenomenon, the condensed material was collected from the walls of the flashover chamber, and samples of the smoke and its acetone extract were subjected to pyrolysis-gas chromatography in a helium atmosphere at 1000°C. Pyrograms of the orange smoke and its acetone extract are illustrated in Figures 5 and 6, respectively. A comparative pyrogram of unretarded polyurethane foam is in Figure 7.

The pyrograms were obtained using 0.9 mg of sample indicating the sensitivity of the flame ionization detector. The pyro-

grams are generally comparable in terms of major identified components with the typical chromatogram obtained for the pyrolysis gas-air mixture, Figure 3. However, it should be noted that for the pyrograms pyrolysis was in a helium atmosphere in a relatively small volume greatly improving the accuracy and detectability of low concentration components.

A major problem in gas analysis in the flash cell results from the low total concentration of products in air. In both cases however identification of additional components in the complex gas mixture will require a mass spectrometer. Quantitative accuracy has been limited by the necessity of using peak heights rather than areas due to lack of a good integrator. In the case of the FID the digital integrator has not performed well with the complex multicomponent mixtures encountered here. Cell design changes would also improve analytical accuracy and this would include sealed end windows and redesigning of sampling ports. The orange smoke and its acetone extract were also analyzed by infrared spectroscopy. Figures 8 and 9 show the infrared spectra of the two samples at 1% in KBr discs. A more detailed infrared spectrum of the acetone extract of the orange smoke was obtained as its solution in carbon tetrachloride in Figure 10.

The large amount of scatter indicated by the low I_0 background in the short wavelength region of the spectrum appears to be

typical of these materials and prevents higher concentrations of sample from being used in the KBr. The spectrum in CCl_4 solution does not show improved resolution, Figure 10, where the upper curve is a very thin capillary film. The curves suggest that the bulk of the smoke is the isocyanate portion of the polyurethane, the polyol fraction being lost in the low temperature ranges. This should be confirmed by further analysis.

A sample of orange smoke was subjected to microanalysis to compare its elemental composition with that of the original polyurethane foam. The results are listed in Table 4. The elemental analysis indicates decreases in the carbon and hydrogen contents as expected from the formation and release of primarily hydrocarbons in the low temperature range. The increase in nitrogen reflects the fact that the nitrogenous compounds are released in the higher temperature range.

The smoke appears to be particulate, coated with a tar-like material which precludes redispersal of the material in air. The elemental analysis does confirm, however, the gas chromatographic analysis that the initial low temperature pyrolysis results in hydrocarbons (C and H compounds only) of low molecular weight plus the smoke.

4.4 Intercomparison of Materials - Flash Fire Potential

A number of polymers were compared in the flash fire cell to determine the magnitude of the differences, if any, obtainable with the present cell configuration. Weighed samples of the materials were heated using identical rates and timing the onset of smoke development and flash fire. These tests were conducted with the cell in a vertical position with the ignition source near the bottom. The results are presented in Table 5 where the times listed are average values of two or more experiments. In each case except for the latex, which showed spontaneous ignition, the high voltage ignition source was turned on at the beginning of heating. This was also done for the latex but spontaneous ignition occurred near the sample surface. The ranking of materials in Table 5 is as expected with the latex and urethanes developing a flash fire most readily.

5.0 SUMMARY AND RECOMMENDATIONS

5.1 Gas Analysis and Smoke Characterization

Previous studies of urethane decomposition have emphasized high temperature inert atmosphere decomposition of the polymer. The low temperature decomposition products have been determined including hydrogen, CO, and hydrocarbons through propylene. Additional work, particularly mass spectrometric, is required to establish the role of the smoke in the flash fire. We have been unable to produce the flash fire with the smoke

filtered out. Propylene, with a lower flammability limit of about 2.8% has not been eliminated as a possible contributor. Methane, hydrogen, and carbon monoxide have been eliminated due to their very low concentrations. A third possible factor in the flash fire are the higher molecular weight hydrocarbons. Evidence to date suggests the smoke produced is, in some circumstances, essential to produce flashover. Additional experimentation is required to better define the role of smoke in the flash fire.

5.2 Development of Flash Fire Cell

The laboratory model has performed well although optimized only in terms of cell orientation. The lower flammability limit varies with the orientation of the cell in the gravitational field [13] with the lowest values obtained with a vertical tube and the ignition source near the bottom.

Additional work required is:

- a. evaluation of other ignition sources. This would include piloted ignition.
- b. determination of optimum sample weight to cell volume ratio.
- c. comparison with other test methods.

Comparison with other test methods would include TGA and DSC data for the same samples. Intercomparison of a greater vari-

ety of urethanes would be valuable since the present cell does not discriminate between the fire retarded and unretarded foams described in Section 3.1. This may in part be due to a loss in retardant in this particular batch of foam. If a significant difference does exist in flash fire potential cell modifications should be attempted to improve the resolution of the system.

6.0 REFERENCES

- [1] Gross, D., Fire Growth and Flashover in Model Enclosures Simulating Airplane Cabins, NBS Report 9931, (October 4, 1968).
- [2] Gross, D., Fire Growth and Flashover in Model Enclosures, #2, NBS Report 10083, (September 11, 1969).
- [3] Gross, D., Loftus, J. J., Lee, T. G., and Gray, V. E., Smoke and Gases Produced by Burning Aircraft Interior Materials, Building Science Series 18, (February 1969).
- [4] Waterman, T. E., Fire Technology, 4, 25 (1968).
- [5] Marcy, John F., Air Transport Cabin Mockup Fire Experiments, Report No. FAA-RD-70-81.
- [6] Zabetakis, M. G., Flammability of Combustible Gases and Vapors, Bureau of Mines Bulletin 627, 1965.
- [7] Abbott, J. C., Fire Journal, 65, 88 (1971).
- [8] McCarter, R. J., NBS Special Publication 338, pp. 137-150 (1972).
- [9] David, D. J., and Staley, H. B., Analytical Chemistry of Polyurethanes (High Polymer Series Monograph), Vol. XVI, Part III, Wiley-Interscience, New York 1969.
- [10] Murphy, E. B., and O'Neil, W. A., SPE Journal 18, 191 (1962).
- [11] McNair, H. M., and Bonelli, E. J., Basic Gas Chromatography, p. 147, 5th Edition, Consolidated Printers, Berkeley, California, 1969.
- [12] Takeuchi, T., et al., J. Gas Chromatography, 6, 542 (1968).

- [13] Lewis, B., and von Elbe, G., Combustion, Flames, and Explosions of Gases, p. 316, Academic Press, Inc., New York, 1961.

Table 1

Weight Percent Composition of
Polyurethane Pyrolysis Products in Air

	Sample			
	11A	11B(a)	12(b)	13
H ₂	---	trace	trace	trace
CH ₄	0.1 ^(d) (0.15) ^(e)	0.2 (0.14)	0.1 (0.13)	0.2 (0.45)
CO	0.1 (0.15)	0.5 (0.6)	---	1.0 (1.2)
O ₂ + Ar ^(f)	22.6 (19.0)	21.7 (19.6)	23.2 (19.5)	19.1 (19.0)
N ₂ ^(f)	77.2 (68.8)	77.6 (73.6)	76.6 (68.0)	79.6 (82.7)
				15(c)

				0.1 (0.16)
				1.8 (1.7)
				19.2 (18.7)
				78.8 (79.3)

(a) after flashover, all other runs before flashover

(b) typical commercial sample, all other runs FAA sample (unretarded)

(c) electrical furnace heat, all other runs external burner

(d) percentage composition calculated by the normalization method

(e) figures in parenthesis are estimated values by the calibration method

(f) composition of air (weight percent): N₂ 75.5, O₂ 23.15, Ar 1.29, CO₂ 0.05

Table 2
Polyurethane Pyrolysis Products
(Peak identification based on retention times)

Peak (Flame Ionization Detector)	Sample				
	11A	11B(a)	12(b)	13	15(c)
A (CH ₄)	1	1	1	1	1
B (H ₂ C = CH ₂ , HC≡CH)	0.16	0.31	0.07	0.25	0.2
C (H ₃ C-CH ₃)	0.06	0.04	0.03	0.03	0.05
D (H ₃ C-CH = CH ₂)	0.60	0.25	0.36	0.45	0.49
E unidentified	0.43	0.13	0.66	0.42	0.26
F (H ₃ C-CO-CH ₃)	0.28	0.10	0.46	0.23	0.16
CO ₂ /air (d)	0.008	----	----	0.005	0.009
H ₂ O (d)	+	+	+	+	+

a, b, c - See Table 1

d - thermal conductivity detector

Table 3
Lower Limits of Flammability
of
Pyrolysis Products in Air¹

gas	L_{25}^2
Hydrogen (H_2)	4.0
Carbon monoxide (CO)	12.5
Methanol (CH_3OH)	6.7
Methane (CH_4)	5.0
Ethane (H_3C-CH_3)	3.0
Ethylene ($H_2C=CH_2$)	2.7
Acetylene ($HC\equiv CH$)	2.5
Acetone ($H_3C-CO-CH_3$)	2.6
Propylene ($H_3C-CH=CH_2$)	2.4
Propane ($H_3C-CH_2-CH_3$)	2.1

¹Reference 6.

²Volume percent at 25°C and atmospheric pressure

Table 4

Elemental Analysis of the Orange Smoke
and Polyurethane Foam (a)

Sample	C%	H%	N%	O% ^(b)
orange smoke	60.2	7.5	9.4	22.9
polyurethane foam	63.0	8.9	5.6	22.5

(a) maximum limits of uncertainty are $\pm 0.3\%$.

(b) oxygen percentage obtained by difference.

Table 5
Intercomparison of Materials - Flash Fire Potential

Material (a)	Time	
	Visual Appearance (b) of Smoke	Flashover (c)
Latex Foam (d)	40 sec	1 min 15 sec
Polyurethane Foam	50 sec	1 min 50 sec
Polyethylene	50 sec	3 min 30 sec
Acrylic Resin	3 min 20 sec	4 min
PVC (e)	55 sec	none
Cellulose (f)	1 min 50 sec	none

(a) 0.3 g samples

(b) The variation in time of appearance of smoke did not exceed ± 5 seconds except for acrylic resin where the range of variation was ± 10 seconds.

(c) Time of occurrence of flashover phenomenon varied within ± 10 seconds for all samples except polyethylene where the variation was within $\pm 1/2$ minute.

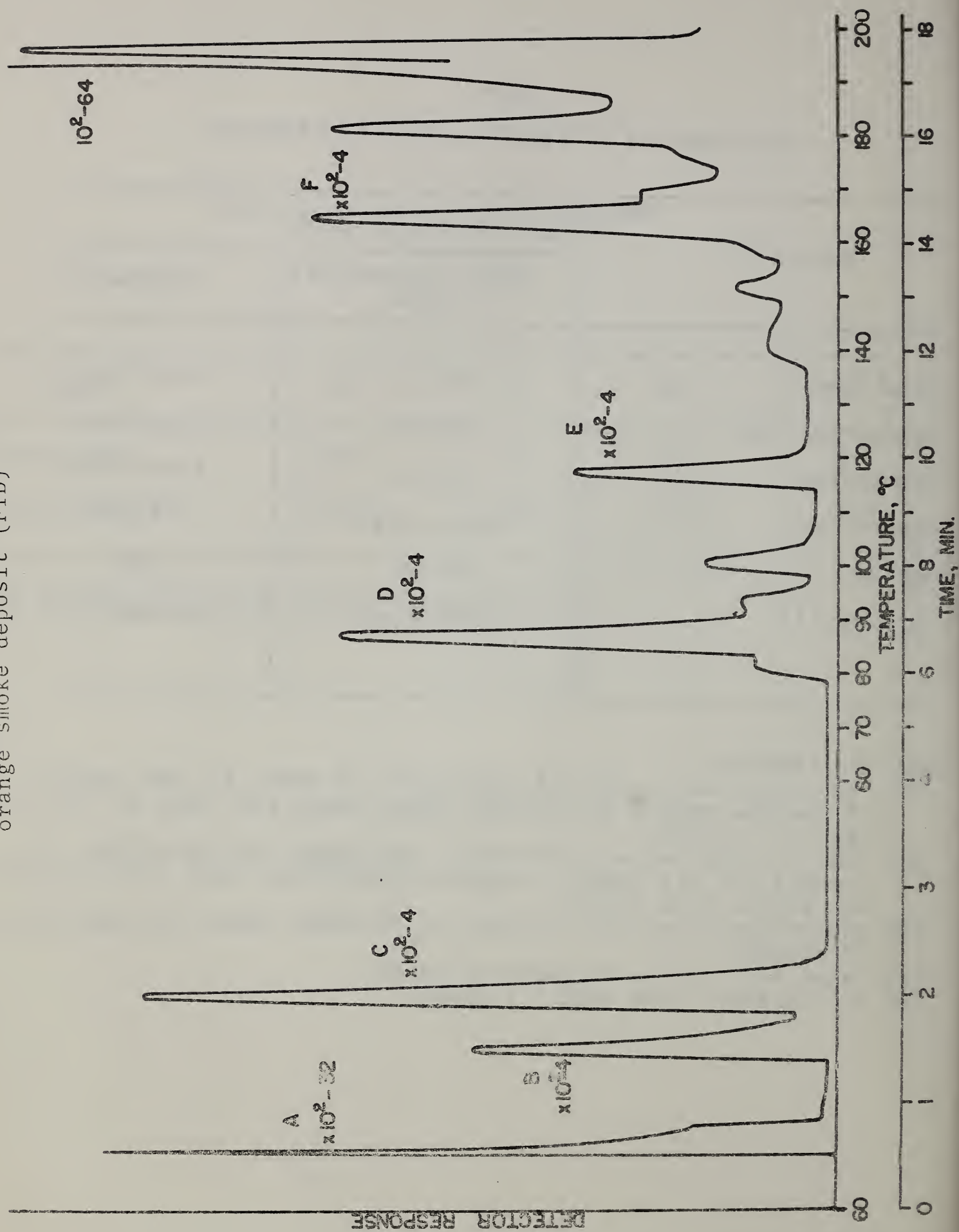
(d) Spontaneous ignition of gases at the heat source in approximately 50 seconds.

(e) Gases burn in the vicinity of spark.

(f) No flashover even with 1 g sample.

Figure 6

Pyrogram of acetone extract of
orange smoke deposit (FID)



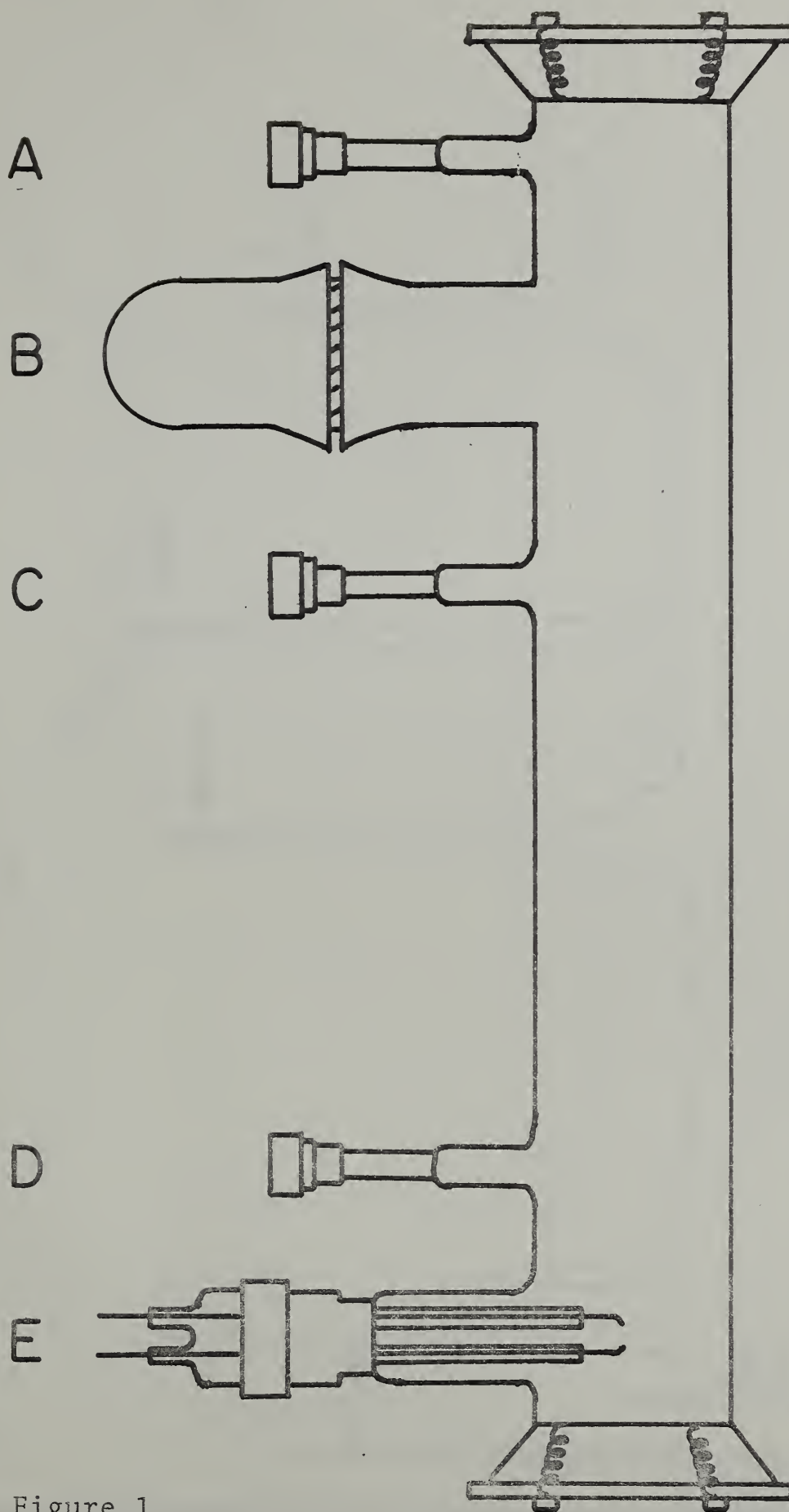
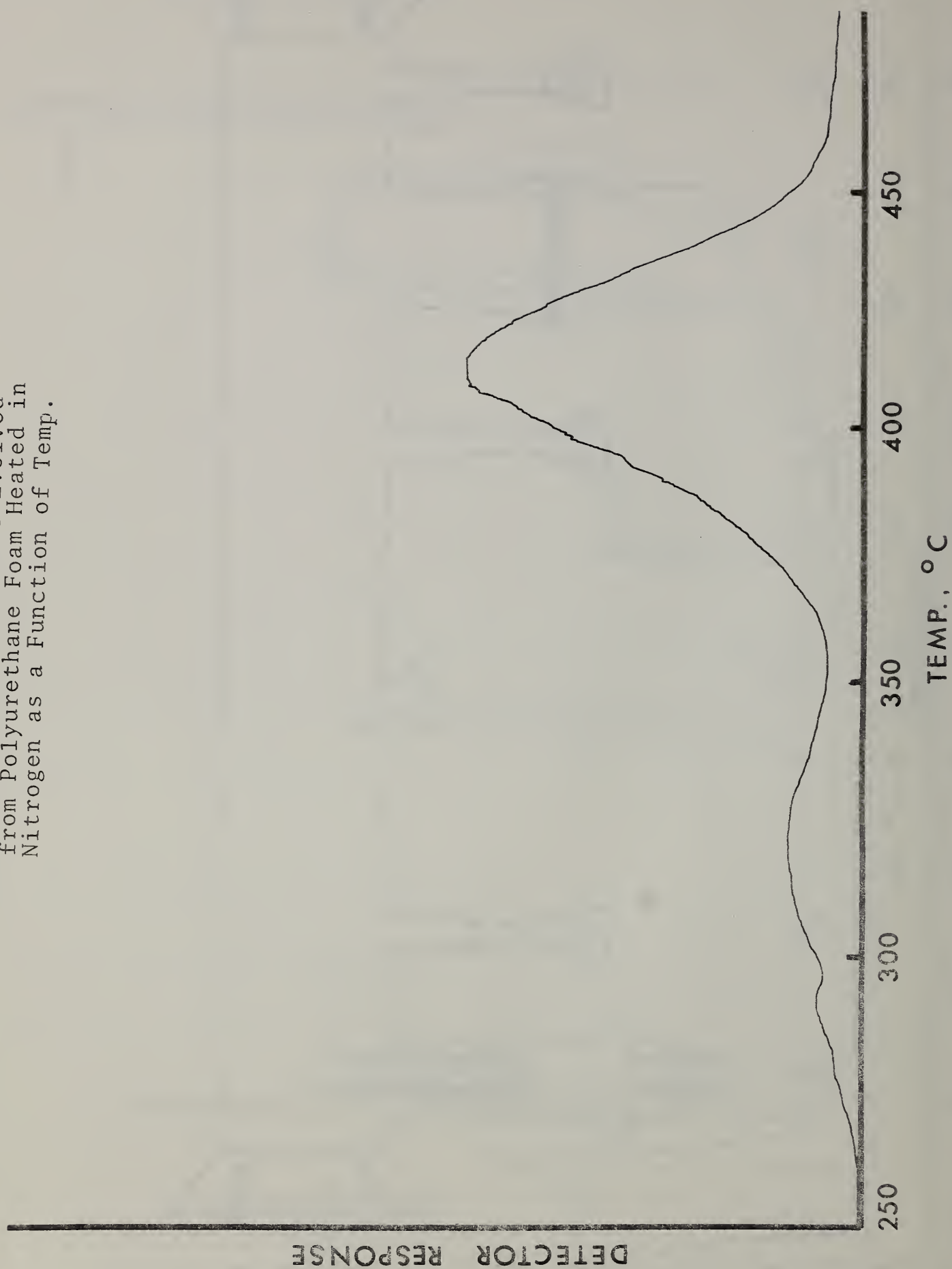


Figure 1

Schema of Flash Fire Cell

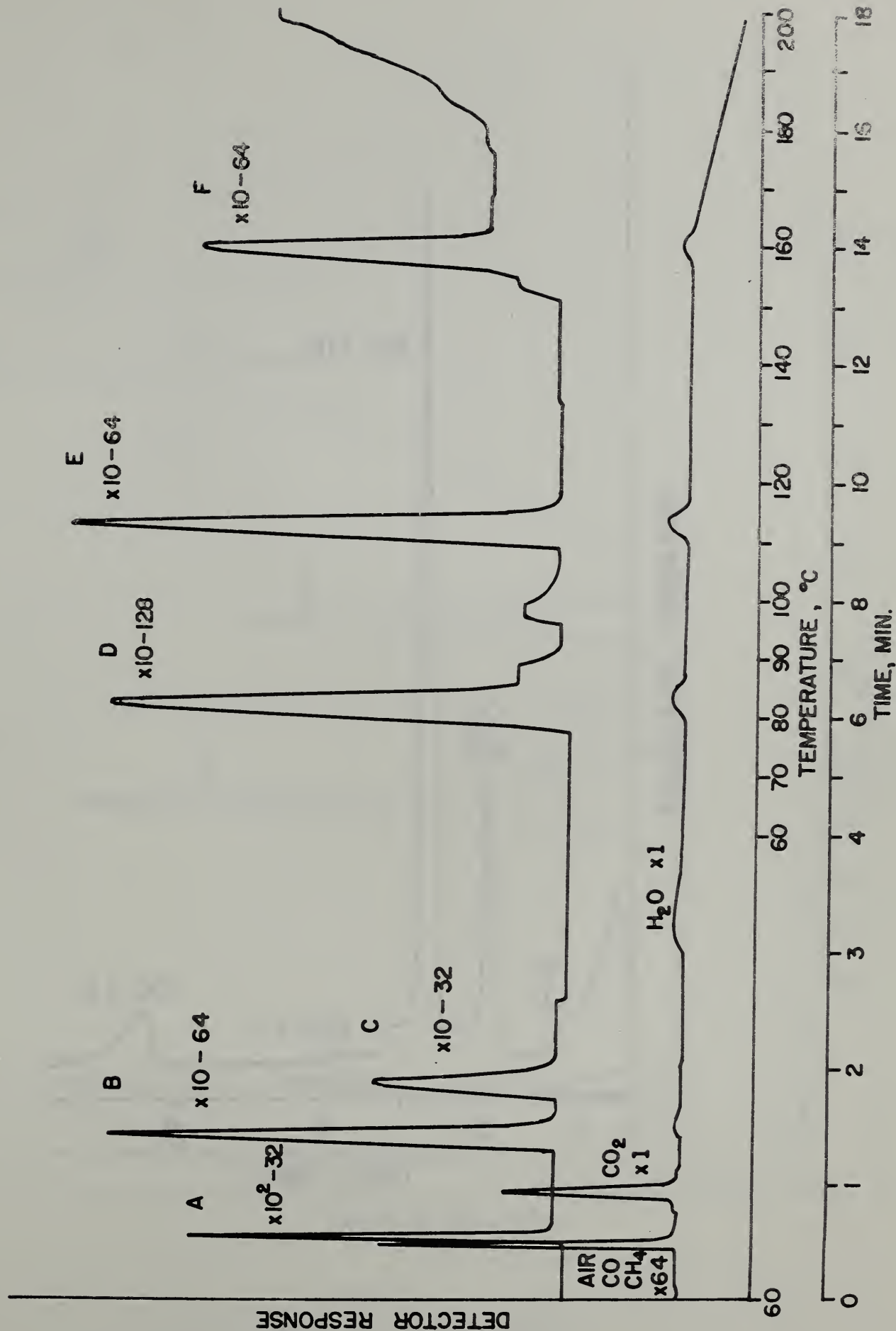
Figure 2

Total Combustible Gases Evolved
from Polyurethane Foam Heated in
Nitrogen as a Function of Temp.



Chromatograms of flexible foam decomposition products in air before onset of flash fire. (FID - upper curve and TC - lower curve). See Table 2 for identification of peaks. Attenuation factors used for reducing the output signal are listed next to each peak (for example - to obtain the absolute signal response for peak A, the peak height must be multiplied by 32×10^2 or 3200).

Figure 3



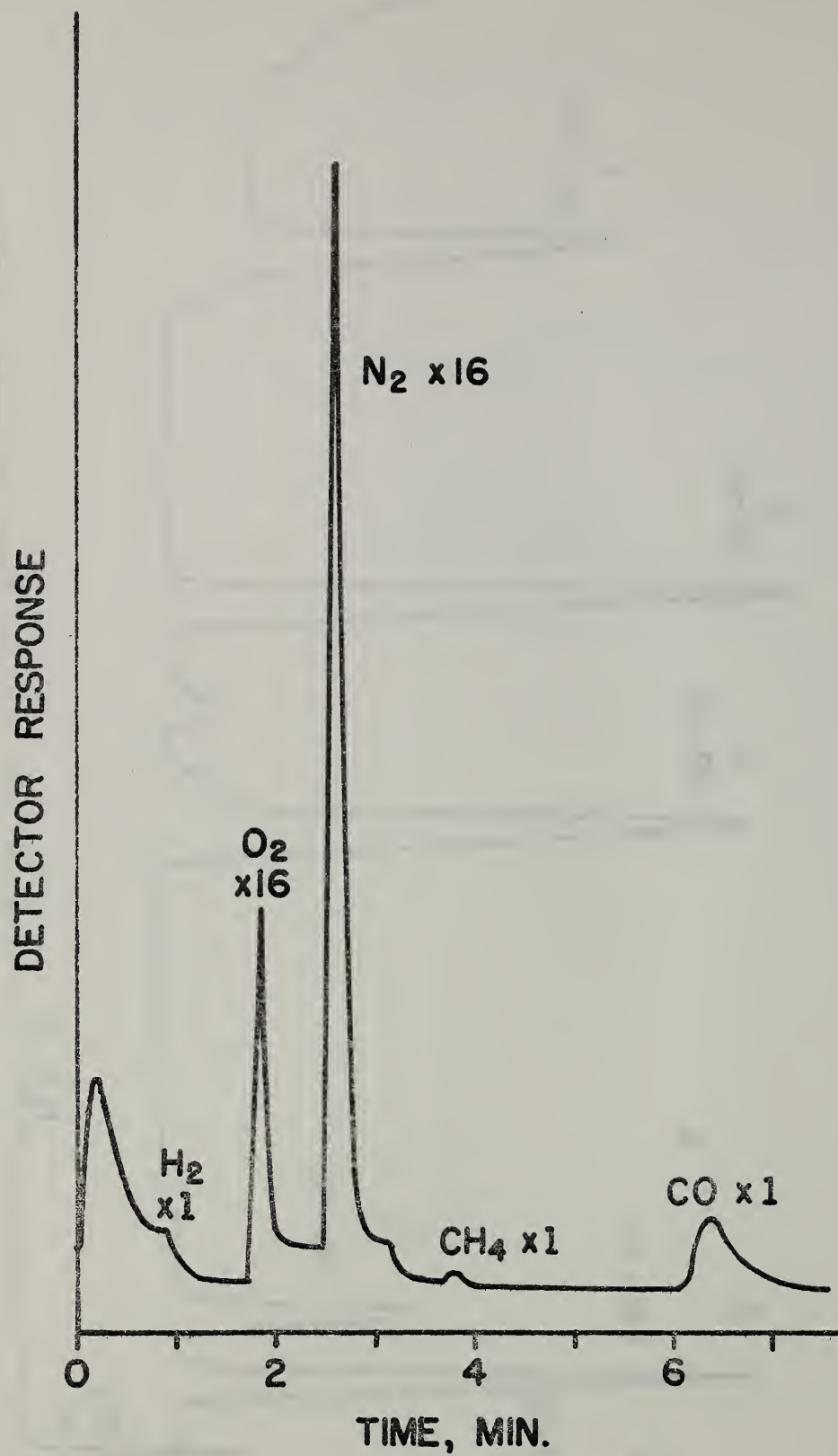


Figure 4
Chromatogram of same mixture as
Figure 3, but with "air" peak re-
solved only (TC).

Figure 5

Pyrogram of orange smoke deposit
from flexible urethane (FID -
upper curve and TC - lower curve).

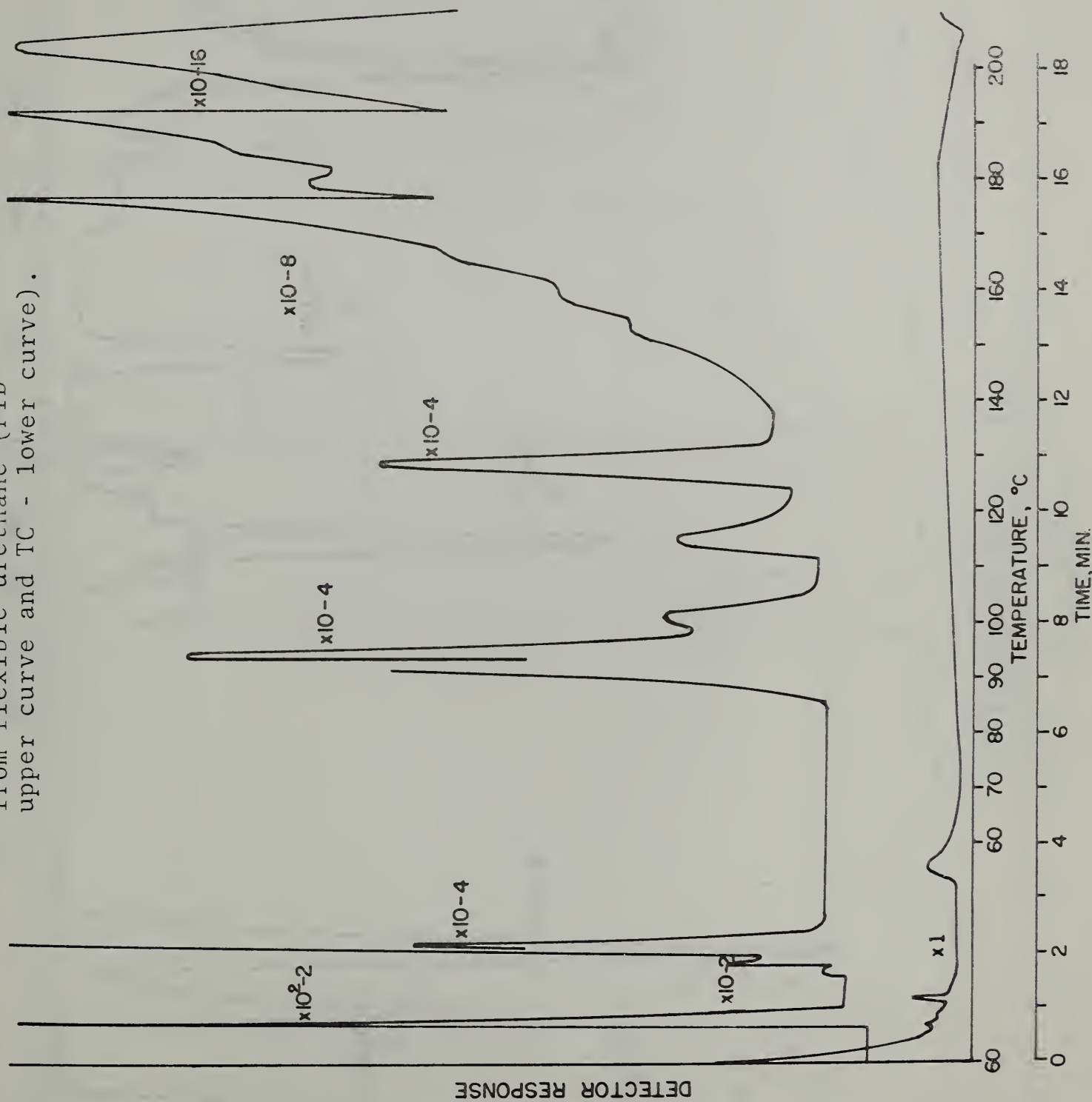


Figure 6

Pyrogram of acetone extract of
orange smoke deposit (FID)

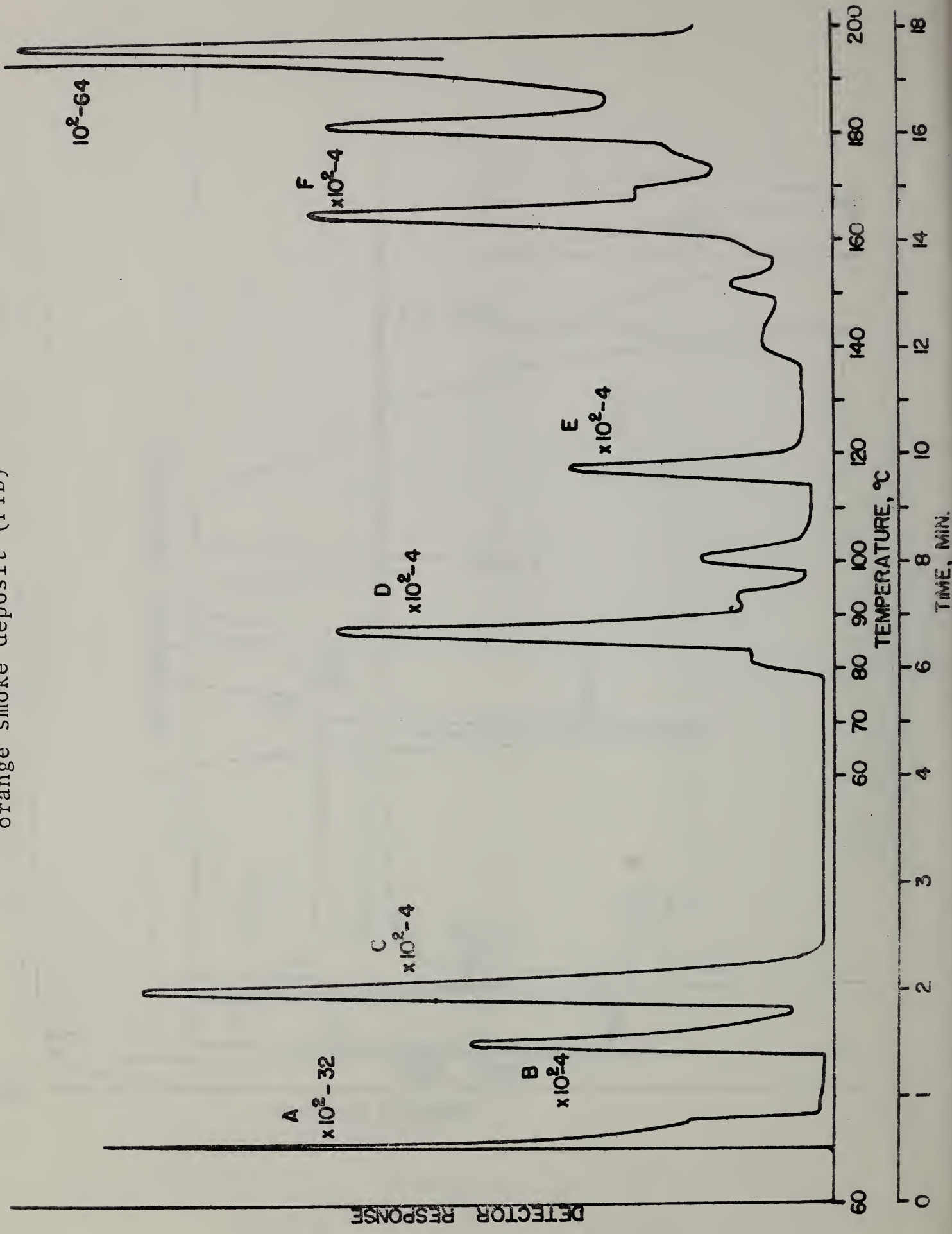


Figure 7
Pyrogram of original unretarded
urethane foam (FID - upper curve
and TC - lower curve).

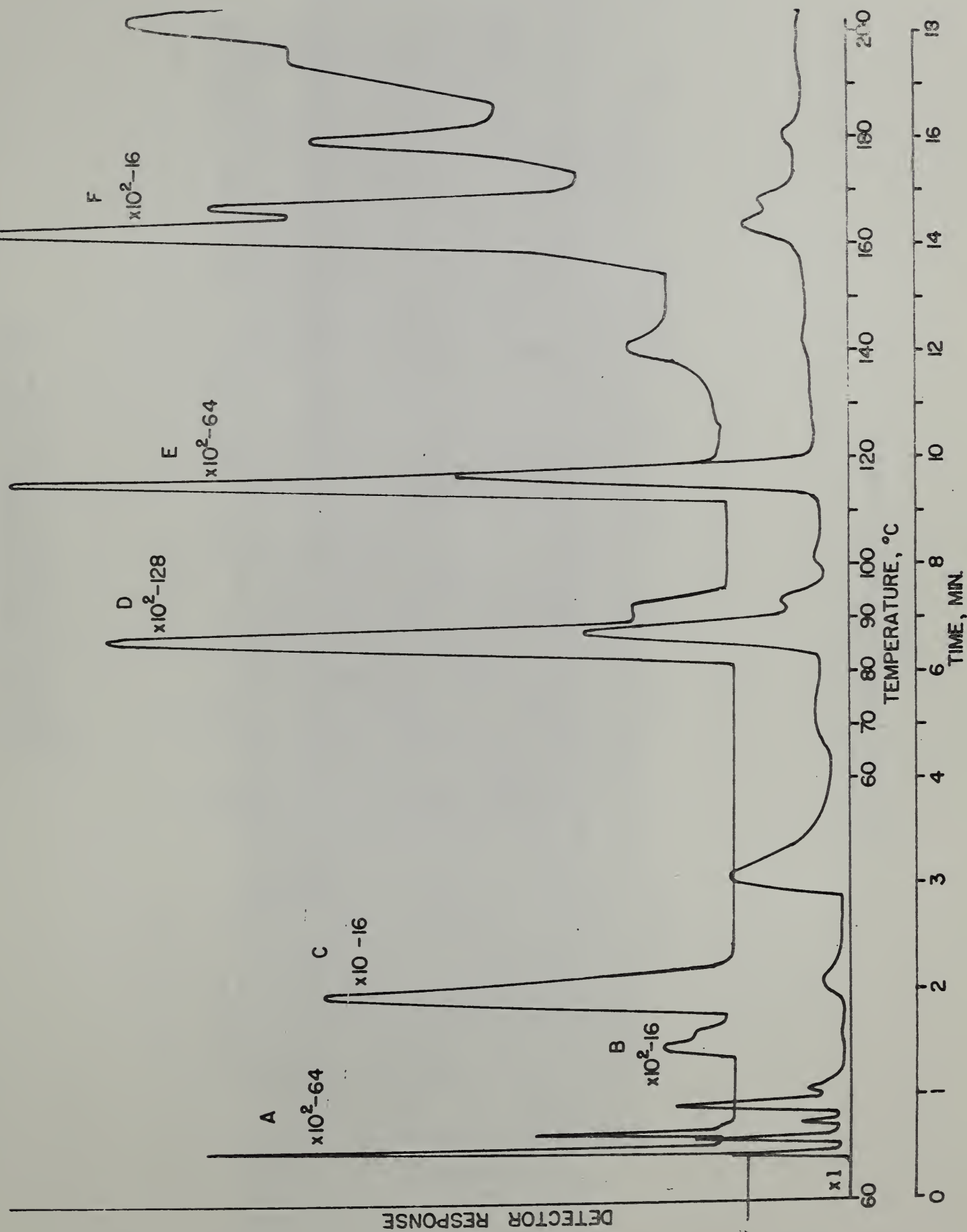


Figure 8
Infrared spectrogram of smoke
condensate in KBr.

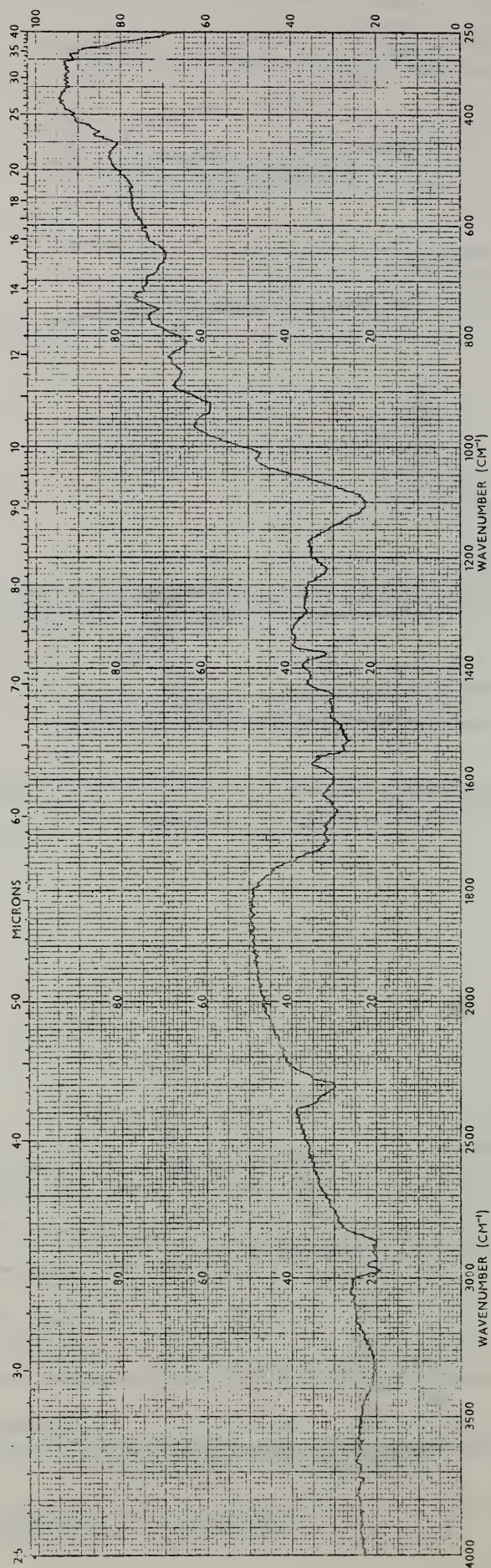


Figure 9
Infrared spectrogram of acetone
extract of smoke condensate in
KBr.

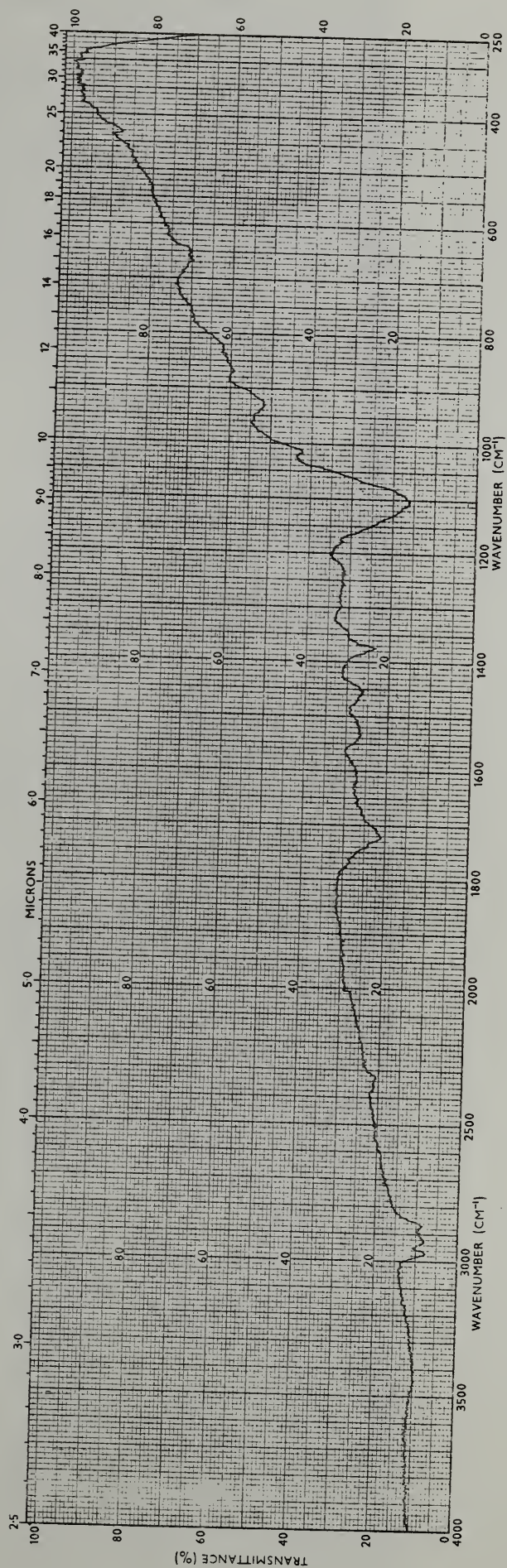


Figure 10

Infrared spectrogram of acetone
extract of smoke condensate in
 CCl_4 (*solvent absorption).

